

Influence of Petrochemical Installations Upon PAH Concentrations at Sites in Western Saudi Arabia

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4 **INFLUENCE OF PETROCHEMICAL**
5 **INSTALLATIONS UPON PAH**
6 **CONCENTRATIONS AT SITES IN**
7 **WESTERN SAUDI ARABIA**

8
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30 **ABSTRACT**

31 Measurements of 16 polycyclic aromatic hydrocarbon (PAH) congeners (particles and vapour) have
32 been made at three sites over a distance of 230 km on the Red Sea coast of Saudi Arabia. The data
33 have been pooled with an earlier dataset from three sites in the city of Jeddah, with one urban site
34 common to both studies. The concentrations and congener profiles are broadly similar for the two
35 measurement campaigns at the common site. Coefficients of Divergence have been calculated and
36 show more substantial differences between the sites within the city of Jeddah than are found
37 between the sites to the north of the city which emphasises the strong concentration gradients within
38 Jeddah in comparison to those found in the atmosphere of the coastal sites to the north of the city.
39 A sub-set of data corresponding to days on which the air mass travelled from the northwest parallel
40 with the Red Sea coast, hence linking the three sites, showed a progressive reduction in
41 concentrations as the air mass travelled towards the southeast, which is attributed to emissions from
42 a large source area to the northwest of the sampling sites and either atmospheric dilution or
43 chemical reaction accounting for a progressive reduction in concentrations with advection of the air
44 mass. The congener profile is very similar to that identified in earlier work relating to oil refinery
45 emissions and is consistent with the major petrochemical installation at Yanbu contributing
46 substantial emissions to the atmosphere which are advected to downwind sites.

47

48 **Keywords:** Polycyclic aromatic hydrocarbons; spatial analyses; atmospheric concentrations;
49 petrochemical works; Saudi Arabia

50

51 INTRODUCTION

52 Polycyclic aromatic hydrocarbons are a group of compounds emitted to the atmosphere from a wide
53 range of combustion processes. There are many compounds within the group, but conventionally a
54 small number are commonly analysed – most often the 16 compounds specified by the US
55 Environmental Protection Agency (Sun et al., 1998). The main driver for measurement is concern
56 over the health risk posed by the PAH mixture, which is listed by IARC as a Class 1 human
57 carcinogen (IARC, 2010). Several congeners within the group contribute to that toxicity and
58 relative potency factors have been proposed by a number of workers (reviewed by Delgado-Saborit
59 et al., 2011). Both the World Health Organization and the European Commission use
60 benzo(a)pyrene (BaP) as a marker for the mixture, as this compound typically accounts for a
61 substantial proportion of the carcinogenic potential of the entire mixture (Delgado-Saborit et al.,
62 2011). While the WHO publishes slope factors relating cancer risk to exposure concentrations but
63 no guideline value (WHO, 2000), the European Union has adopted a target value of 1 ng m^{-3} of
64 BaP. A review of the health risk of PAH exposure in the context of indoor air (WHO, 2010) has
65 highlighted health outcomes other than cancer for which there is strong evidence of a contribution
66 from PAH. Bae et al. (2010) have shown an association between PAH exposure, measured by a
67 biomarker, and oxidative stress, which is a precursor to disease. According to Trasande et al.
68 (2015), children living close to an oil refinery, which was a known source of PAH, showed a
69 significant increase in symptoms of pre-hypertension. Kim et al. (2013) reviewed the human health
70 effects of airborne PAH exposure, discussing both acute and chronic health effects.

71

72 As the PAH mixture is a genotoxic carcinogen, there is no wholly safe level of exposure and a
73 consequent need exists to minimise exposure from all sources. PAH emissions derive from
74 combustion sources such as gasoline and diesel engine exhaust, wood smoke and food cooking, as
75 well as from industrial processes such as steel production and anode baking in aluminium
76 production, and from the evaporation of fossil fuels (Baek et al., 1991; Mastral and Callen, 2000).

77 Since the development of cost-effective abatement strategies requires a sound knowledge of
78 individual source contributions to ambient concentrations, there is a pressing need for source
79 apportionment studies, such as that conducted by Jang et al. (2013) using data from the United
80 Kingdom PAH monitoring network and Wang et al. (2015) using a large dataset collected at a
81 megacity in China. In addition to the application of Positive Matrix Factorization to a multi-site,
82 multicomponent dataset, Jang et al. (2013) used spatial distribution analysis to infer source
83 contributions. The differences in concentrations between paired sites were used to infer source
84 contributions, which could be compared with emissions inventory data. Site pairs included
85 roadside/urban background pairs and industrial/urban background pairs of sites. Mari et al. (2010)
86 also made a qualitative comparison of congener profiles between urban and rural sites, and
87 compared a road traffic profile with an urban background concentration profile, but did not use
88 quantitative measures of difference.

89

90 A factor to consider in analysing ambient air measurements of PAH is that the compounds are
91 reactive in the atmosphere at differing rates leading to degradation, and a consequent change occurs
92 in the ratios of compounds from those emitted at source (Keyte et al., 2013). A further
93 consideration is that PAH are semi-volatile compounds which actively partition between the vapour
94 and condensed phases, and to fully understand their airborne concentrations it is necessary to
95 measure both phases (Yamasaki et al., 1982). Receptor modelling is also likely to generate
96 misleading results unless the sum of both phases is used in the model (Harrison et al., 1996; Xie et
97 al., 2013; Gao et al., 2015).

98

99 There have been relatively few measurements of PAH in countries from the Middle Eastern region.
100 Alghamdi et al. (2015a) review data from Assiut, Egypt (Abdallah and Atia, 2014), Giza, Egypt
101 (Hassan and Khoder, 2012), Tehran, Iran (Halek et al., 2010), Kuwait (Gevao et al., 2006) and
102 Zonguldak, Turkey (Akyuz and Cabuk, 2010) as well as measurements from two locations in Saudi

103 Arabia: Makkah (Habeebullah, 2013) and Riyadh (El-Mubarek et al., 2014). These show a huge
104 diversity in concentrations, with concentrations reported from Egypt and Iran far exceeding those
105 from sites in Jeddah, Saudi Arabia (measured by Alghamdi et al., 2015a), and those from Kuwait
106 falling below the Jeddah data. Both the studies of Habeebullah (2013) and El-Mubarak et al. (2014)
107 report very high PAH concentrations; the latter reported average benzo(a)pyrene of 400 ng m^{-3} ,
108 which is so high as to require independent confirmation. Due to the very different climate, and
109 availability of fuels, it is anticipated that PAH sources may be very different in the Middle Eastern
110 region from that in temperate western countries. It is anticipated that there would be little use of
111 coal or wood as fuels, but greater dependence upon petroleum-based products.

112
113 The anticipated dominance of petroleum based sources is borne out by a receptor modelling study
114 conducted in Saudi Arabia. In a study of PAH measured at three sites in Jeddah, Saudi Arabia,
115 Alghamdi et al. (2015a) used PMF to apportion PAH to three factors representing traffic emissions,
116 industrial sources, especially an oil refinery, and oil combustion. The purpose of this research is to
117 extend the geographic coverage of PAH concentrations and source attribution well beyond Jeddah
118 and Riyadh for which data are already available into that part of the western coast which contains
119 extensive petrochemical industry activity. In this paper we report further measurements from one
120 of the sites used by Alghamdi et al. (2015a) – Site C in that paper – and over the same campaign
121 period from two further sites up to 230 km to the north of Jeddah. These new data include
122 measurements from two sites which substantially increase the spatial coverage, and were collected
123 so as to test for spatial trends in concentration within the prevailing air mass movements from
124 north-west towards south-east along the Red Sea coast (see Figure 1). They also include a rural site
125 for which very few data are available in this region.

129 **EXPERIMENTAL**

130 **Sampling Sites**

131 These are shown in Figure 1.

132

133 **FIGURE 1 HERE**

134

135 **Site A (Refinery) (21.4439°N; 39.2005°E)** is a primary school situated in a highly populated
136 economically disadvantaged residential area in the south of the city of Jeddah, about 700 metres
137 east of the Jeddah oil refinery, and close to the Port of Jeddah.

138

139 **Site B (Ring Road) (21.4727°N; 39.2755 °E)** is also a primary school in the eastern part of Jeddah,
140 about 150 metres from the heavily trafficked Al-Haramian ring road.

141

142 **Site C (Abhur) (21.7572°N; 39.1147°E)** is located in the grounds of a research institute on the Red
143 Sea coast to the west of major roads. It is in the northern suburbs of the major city of Jeddah
144 (population 5 million), with the King Abdulaziz international airport to the east (inland). The site is
145 approximately 130 km to the SE of Rabegh.

146

147 **Site D (Rabegh) (22.8122°N; 39.0664°E)** is a site located about 1 km from the residential areas of
148 this substantial city, which has appreciable local industry. The sampling site is ca. 500 metres east
149 of the coastal road. It is approximately 100 km SSE of Rayes.

150

151 **Site E (Rayes) (23.5756°N; 38.6058°E)** is a sparsely developed area with little road traffic and no
152 appreciable local sources. The sampling site is located about 950 metres inland (east) of the coastal
153 road, and 25-50 km SSE of the large industrial complex in the region of Yanbu.

154

155 Wind trajectories in western Saudi Arabia often travel parallel to the coast from an approximately
156 north-westerly direction. Consequently, three sites were selected for air sampling spaced along the
157 coast, to the south east of the major petrochemical plant located south of Yanbu. Thus, air masses
158 travelling parallel to the coast after Yanbu would firstly cross the site at Rayes, some 25-50 km
159 southeast of the industrial activities around Yanbu (see Figure 1). Rayes is in a sparsely developed
160 area and would be expected to experience predominantly regionally polluted air masses, as well as
161 possibly being influenced by emissions from the Yanbu industrial complex. The second site along
162 the coast is Rabegh which is located within a major urban area, with both local road traffic and
163 industrial influences. It is 100 km from Rayes. The third site, Abhur is in the northern suburbs of
164 Jeddah city, about 130 km from Rabegh. Southerly air masses would carry the pollution load from
165 the city, while air masses following the coast from the north-west would cross few areas of
166 population between Rabegh and Abhur. The area is mainly residential with local traffic influences,
167 but no industry, other than that to the south within Jeddah. The city of Jeddah has both high traffic
168 density and major fixed emission sources including an oil refinery and a desalination plant which
169 burns fuel oil.

170

171 In order to carry out an effective Lagrangian test of compositional change, the sampling of air
172 masses at Sites E, D and C was staggered to allow for the atmospheric transport of air masses.
173 Samples were hence initiated sequentially at 05.00 (Site E), 11.00 (Site D) and 17.00 (Site C) local
174 time, and each continued for 24 hours.

175

176 **Dates of Sampling**

177 The first campaign was at Sites A, B and C, and daily 24-hour samples were collected
178 simultaneously at all sites between 23 February 2013 and 23 April 2013. Peak daily temperatures
179 over this period ranged from 26 to 30°C. The data from that campaign have been reported as part of
180 a study of brachial artery distensibility in relation to pollutant exposure by Trasande et al. (2015), a

181 receptor modelling study by Alghamdi et al. (2015a), and a study of urinary PAH metabolites by
182 Alghamdi et al. (2015b). The second campaign took place at Sites C, D and E from 16 June 2013 to
183 7 July 2013 and 17 September to 1 October 2013 (summer) and 23 December 2013 to 30 January
184 2014 (winter). Peak hourly temperatures ranged from 38-47°C (summer) and 23-30°C (winter).

185

186 **Sampling Instruments**

187 Samples were collected using a “pesticide” sampler (TE-PUF, Tisch Environmental Inc.) which
188 draws air (240-300 m³ per day) through a TSP inlet onto a quartz microfibre filter (TE-QMA4;
189 10.16 cm) to collect particulate matter, followed by an adsorbent polyurethane (PUF) substrate to
190 collect vapour phase compounds.

191

192 **Chemical Analysis**

193 Prior to sampling, the filters were preheated at 400 °C for 48 h in a box furnace, wrapped in a clean
194 preheated foil, placed in a cardboard box and sealed in an airtight metallic container. The PUF
195 substrates were pre-cleaned prior to their use in the field by immersing in 100 mL of
196 dichloromethane (DCM) and ultrasonicing at 20°C for 30 min. The solvent was then drained and
197 the PUF substrates were left to dry in a sealed metal container under a stream of nitrogen. The clean
198 and dry PUF substrates were subsequently sealed in airtight plastic bags and stored in the freezer.
199 Once exposed, the filter and PUF substrates were wrapped separately with a clean preheated foil,
200 enclosed in airtight plastic bags and stored at approximately -18°C.

201

202 Samples were analysed for 16 PAH using the methodology described previously (Delgado-Saborit
203 et al., 2010; 2013). Briefly, filter and PUF substrates were spiked with 1000 pg μL^{-1} deuterated
204 internal standards for quantification. Nine deuterated compounds were used, covering the volatility
205 range from acenaphthylene-d₈ to benzo(ghi)perylene-d₁₂. A recovery standard, p-terphenyl-d₁₄ was
206 also added using a solution of 2000 pg μL^{-1} . Filters were immersed in dichloromethane (DCM) and

207 ultrasonicated for 15 min at 20°C. The extract was subsequently dried and cleaned using a
208 chromatography column filled with 0.5 g of anhydrous sodium sulphate (puriss grade for HPLC).
209 The extract was further concentrated to 50 µL under a gentle N₂ flow. PUF substrates were
210 immersed in 100 mL of DCM and ultrasonicated for 20 min at 20°C. The sample was then
211 concentrated to 10 mL using N₂ and subsequently dried and cleaned as outlined for the filters
212 above.

213

214 Samples were analysed for PAH compounds using Gas Chromatography (6890, Agilent
215 Technologies) equipped with a non-polar capillary column (Agilent HP-5MS, 30 m, 0.25 mm ID,
216 0.25 µm film thickness — 5% phenylpolysiloxane) in tandem with a Mass Spectrometer (5973 N,
217 Agilent Technologies). The precision of analysis was 8±4% (range: RSD, 0.3-9.7%) and the
218 accuracy, expressed as the difference between the measured and true value as a percentage of the
219 true value was 6±4% (range: -6 to 25%). The analytical detection limits varied widely between
220 congeners, and sample detection limits estimated from analysis of blank filters and PUFs all lay
221 well below 1 pg m⁻³ for the 24-hour air samples. Further information regarding the analytical
222 procedure can be found in Delgado-Saborit et al. (2010; 2013). Some of the PUF substrates
223 showed contamination in the later part of the chromatogram making quantification of compounds
224 from benzo(e)pyrene to coronene unreliable. As these compounds are typically > 90% particulate
225 (Alghamdi et al, 2015a) the vapour component has not been quantified, therefore implying an
226 underestimation of up to 10% in concentration of these compounds.

227

228 **RESULTS AND DISCUSSION**

229 Mean concentrations of PAH for each congener and each site appear in Table 1, and
230 diagrammatically in Figure 2. Phase partitioning was considered in detail in our earlier study
231 (Alghamdi et al., 2015a), and was found to be similar in this dataset. The bars marked Site A, B and
232 C in Figure 2 derive from data from the first campaign, while the data for Rayes (site E), Rabegh

(site D) and Abhur (site C2) are from the second campaign. This shows a clear spatial pattern, with highest concentrations at Site A which is strongly influenced by the Jeddah refinery and port, and second highest at Site B where the main influence is from road traffic. Concentrations at Site C, Abhur on the northern boundaries of Jeddah, can be compared between the first and second campaign. It can be seen from Figure 2 that concentrations at the Abhur site (C1 and C2) were broadly similar in the two campaigns.

There are indications in Figure 2 of a concentration gradient in the sense of Rayes (Site E) > Rabegh (Site D) > Abhur (Site C). This was explored further by selecting a sub-set of data corresponding only to those days when the air mass back trajectory ran from north-west to south-east parallel to the Red Sea coast of Saudi Arabia, as in the example trajectory shown in Figure 3. This sub-set corresponds to a total of 14 samples which included all 12 from the summer campaign and 2 from the winter campaign measurements. When averaged (Figure 4), these show a marked gradient in most PAH congeners from Site E (Rayes) > Site D (Rabegh) > Site C (Abhur). This is despite the different characteristics of the sites and the fact that Rabegh may have local source influences, and Abhur is in an area with light local urban traffic. The fact that the highest concentrations are observed at remote Site E (Rayes) is clearly indicative of a major source to the north-west of that site, which is presumably the major petrochemical complex at Yanbu. As the air mass is advected along the Red Sea coastline towards the south-east, concentrations are reduced progressively through atmospheric dispersion/dilution processes and chemical reactions of the PAH (Keyte et al., 2013).

TABLE 1 HERE

FIGURE 2, 3 AND 4 HERE

259 The Coefficient of Divergence is defined as:

$$COD_{fh} = \sqrt{\frac{1}{n} \sum_{i=1}^n \left(\frac{x_{if} - x_{ih}}{x_{if} + x_{ih}} \right)^2}$$

260 In which x_{if} and x_{ih} are the respective concentrations for sampling period i at sites f and h
261 respectively and n is the number of observations. Values of COD for the site pairs measured
262 simultaneously in this study appear in Table 2. Small values of COD are indicative of only small
263 differences in concentrations between sites, while values approaching the theoretical maximum of
264 one reflect large inter-site differences. Comparisons are based upon total (particulate plus vapour)
265 concentrations.

266

267 Data from the first campaign appear in Table 2(a), and show a large divergence between both Site
268 A, close to the Jeddah refinery, and Site B, close to the major highway, and Site C in the relatively
269 unpolluted northern suburbs. Differences between the more polluted Sites A and B are much
270 smaller. With respect to the second campaign and the three more northerly sites, COD values are
271 typically intermediate. The lowest values, representing the greatest similarity between sites are
272 between Site D (Rabegh) and Site C (Abhur). Not unexpectedly, the largest differences are seen
273 between Sites E and C which have the largest spatial separation.

274

275 TABLE 2 HERE

276

277 One sample, collected on 29 September 2013 showed a major elevation in concentrations of all
278 PAH. This was seen both in the particulate and vapour forms, and hence it is considered to reflect a
279 genuine atmospheric phenomenon, and not laboratory contamination of a single sample. It is
280 thought likely to be the result of a single major contribution event close to the Rayes sampling site
281 (E), which showed the greatest elevation in concentrations. For many of the congeners, a lesser
282 elevation was seen on the same sampling date at the downwind Rabegh sampling site. The same

283 general pattern of concentrations at Rayes (site E) > Rabegh (site D) > Abhur (site C) was repeated
284 in this sample, and it has been retained in the averaging process as it does not affect the overall
285 pattern of absolute or relative concentrations appreciably.

286

287 Diagnostic ratios are widely used in source attribution of PAH, although where multiple sources are
288 present, their use is extremely limited (Galarneau, 2008). Diagnostic ratios are also influenced by
289 atmospheric degradation processes (Tobiszewski and Namiesnik, 2012). There appear to be very
290 few published data concerning PAH from petrochemical complexes, but Zhao et al. (2015) report
291 data from eight villages surrounding a large petrochemical complex in Guangzhou, China. They
292 report that ratios of ANT/(ANT + PHE) which fall below 0.1 are typical of a petrogenic source such
293 as a petrochemical works and their data showed ratios within this range. They cite Ravindra et al.
294 (2008) as the source of this information but that paper does not appear to refer to petrochemical
295 sources. There is however support for this ratio to distinguish petrogenic from pyrogenic sources of
296 PAH in the work of Yunker et al. (2002) and Pies et al. (2008). In a recent paper, Dominguez-
297 Morueco et al. (2015) report PAH concentrations measured with passive air samplers in the
298 petrochemical area of Tarragona, Spain. They report a predominance of 3-ring compounds and
299 ratios of ANT/(ANT+PHE) of <0.1. It is notable that ratios of ANT/(ANT + PHE) fell below 0.1 at
300 all of the measurements sites used in our study. This is unsurprising for the sites in Jeddah where
301 there is a petroleum refinery within the boundaries of the city, and Site A was located close to it.
302 The fact that the ratios fell well below 0.1 at the Rayes site, which is downwind of the
303 petrochemical complex at Yanbu is strongly suggestive of the petrochemical complex being the
304 source of the elevated PAH concentrations at Rayes. Alternatively, because of the greater chemical
305 reactivity of anthracene relative to phenanthrene, it may simply be due to degradation of anthracene
306 during airmass transport. Alam et al. (2013) examined ANT/(ANT + PHE) ratios from two sites in
307 Birmingham, UK, one located at roadside and the other at urban background and also calculated a
308 traffic increment from the difference in concentration between the sites. They examined diagnostic

309 ratios and report values for $ANT/(ANT + PHE)$ which are all in excess of 0.1 for the traffic
310 increment. The majority are in excess of 0.1 for the roadside site, but all of the values of this ratio
311 fall below 0.1 for the urban background site which they interpret as due to the atmospheric
312 reactivity of anthracene being greater than phenanthrene and reducing the ratio as the air ages.
313 Consequently, we feel that diagnostic ratios do not give us a definitive indication of the sources of
314 elevated concentrations of PAH at Rayes but that the elevation is consistent with a petrogenic
315 source such as the petrochemical complex upwind at Yanbu.

316

317 There were insufficient samples to carry out a further PMF analysis from the second campaign.
318 However, the congener profile of the PAH can be compared with those of the three source-related
319 factors identified by Alghamdi et al. (2015a). The industrial (oil refinery) factor has substantial
320 concentrations of phenanthrene > pyrene > fluoranthene > anthracene with only very minor
321 amounts of other congeners. This is very similar to the profile seen in Figure 4 for the three sites
322 during the second campaign, when winds were parallel to the coast.

323

324 **CONCLUSIONS**

325 The results of the Coefficients of Divergence calculations show strong gradients in concentration
326 between the heavily polluted sites in southern Jeddah and the background site (Site C, Abhur) in the
327 northern suburbs of the city. This is consistent with conclusions in our earlier work that Sites A and
328 B in the south of Jeddah were heavily influenced by local sources, a refinery and a major highway
329 respectively. Concentration gradients between the sites on the Red Sea coast to the north of Jeddah
330 generate much smaller Coefficients of Divergence indicative of lesser concentration gradients. The
331 steady decline seen in Figure 4 for those days in which the air mass moved from northwest,
332 southeast along the Red Sea coast are consistent with a major source of PAH to the north of the
333 Rayes sampling site. The congener profile is consistent with that source being the large
334 petrochemical works in the vicinity of Yanbu. Figure 4 also shows a steady decline in

335 concentrations as the air mass moves towards the southeast which might be attributable either to
336 progressive dilution with cleaner air or alternatively to reduction in concentrations due to chemical
337 reactions. Without further supporting information, it is not possible to clearly identify the causal
338 factor. Such supporting information might include measurements of a passive (unreactive) tracer
339 compound from which to assess the extent of dilution during transport.

340

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345

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REFERENCES

- Alam, M.S., Delgado-Saborit, J.M., Stark, C., Harrison, R.M., 2013. Using atmospheric measurements of PAH and quinone compounds at roadside and urban background sites to assess sources and reactivity. *Atmospheric Environment* 77, 24-35.
- Abdallah, M.-E., Atia, N., 2014. Atmospheric concentrations, gaseous–particulate distribution, and carcinogenic potential of polycyclic aromatic hydrocarbons in Assiut, Egypt. *Environmental Science Pollution Research* 1-11, doi 10.1007/s11356-014-2746-6.
- Alghamdi, M.A., Alam, M.S., Yin, J., Stark, C., Jang, E., Harrison, R.M., Shamy, M., Khoder, M.I., Shabbaj, I.I., 2015a. Receptor modelling study of polycyclic aromatic hydrocarbons in Jeddah, Saudi Arabia. *Science of the Total Environment* 506-507, 401-408.
- Alghamdi, M.A., Alam, M.S., Stark, C., Mohammed, N., Harrison, R.M., Shamy, M., Khoder, M.I., Shabbaj, I., Göen, T., 2015b. Urinary metabolites of polycyclic aromatic hydrocarbons in Saudi Arabian schoolchildren in relation to sources of exposure. *Environmental Research* 140, 495-501.
- Akyuz, M., Cabuk, H., 2010. Gas-particle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey. *Science of the Total Environment* 408, 5550-5558.
- Bae, S., Pan, X.-C., Kim, S.-Y., Park, K., Kim, Y.-H., Kim, H., Hong, Y.-C., 2010. Exposures to particulate matter and polycyclic aromatic hydrocarbons and oxidative stress in schoolchildren. *Environmental Health Perspective* 118, 570-583.
- Baek, S.O., Field, R.A., Goldstone, M.E., Kirk, P.W., Lester, J.N., Perry, R., 1991. A review of atmospheric polycyclic aromatic hydrocarbons: Sources, fate and behavior. *Water, Air and Soil Pollution* 60, 279-300.
- Delgado-Saborit, J.M., Alam, M.S., Pollitt, K.J.G., Stark, C., Harrison, R.M., 2013. Analysis of atmospheric concentrations of quinones and polycyclic aromatic hydrocarbons in vapour and particulate phases. *Atmospheric Environment* 77, 974-982.
- Delgado-Saborit, J.M., Stark, C., Harrison, R.M., 2011. Carcinogenic potential, levels and sources of polycyclic aromatic hydrocarbon mixtures in indoor and outdoor environments and their implications for air quality standards. *Environment International* 37 383-392.
- Delgado-Saborit, J.M., Aquilina, N., Baker, S., Harrad, S., Meddings, C., Harrison, R.M., 2010. Determination of atmospheric particulate-phase polycyclic aromatic hydrocarbons from low volume air samples. *Analytical Methods* 2, 231-242.
- Dominguez-Morueco, N., Augusto, S., Trabalon, L., Pocurull, E., Borrull, F., Schuhmacher, N., Domingo, J.L., Nadal, M., 2015. Monitoring PAHs in the petrochemical area of Tarragona County, Spain: comparing passive air samplers with lichen transplants. *Environmental Science Pollution Research* doi 10.1007/s11356-015-5612-2.
- El-Mubarak, A.H., Rushdi, A.I., Al-Mutlaq, K.F., Bazeyad, A.Y., Simonich, S.L.M., Simoneit B.R.T., 2014. Identification and source apportionment of polycyclic aromatic hydrocarbons in ambient air particulate matter of Riyadh, Saudi Arabia. *Environmental Science Pollution Research* 21, 558-567.

399 Galarneau, E., 2008. Source specificity and atmospheric processing of airborne PAHs:
400 Implications for source apportionment. *Atmospheric Environment* 42, 8139-8149.
401

402 Gao, B., Wang, X.-M., Zhao, X.-Y., Ding, X., Fu, X.-X., Zhang, Y.L., He, Q.-F., Zhang, Z., Liu,
403 T.-Y., Huang, Z.-Z., Chen, L.-G., Peng, Y., Guo, H., 2015. Source apportionment of atmospheric
404 PAHs and their toxicity using PMF: Impact of gas/particle partitioning. *Atmospheric Environment*
405 103, 114-120.
406

407 Gevao, B., Al-Omair, A., Sweetman, A., Al-Ali, L., Al-Bahloul, M., Helaleh, M., Zafar, J., 2006.
408 Passive sampler-derived air concentrations for polybrominated diphenyl ethers and polycyclic
409 aromatic hydrocarbons in Kuwait. *Environmental Toxicological Chemistry* 25, 1496-1502.
410

411 Habeebullah, T.M., 2013. Risk assessment of poly cyclic aromatic hydrocarbons in the Holy City of
412 Makkah, Saudi Arabia. *International Journal of Environmental Science Development* 4, 139-142.
413

414 Halek, F., Kianpour-rad, M., Kavousi, A., 2010. Characterization and source apportionment of
415 polycyclic aromatic hydrocarbons in the ambient air (Tehran, Iran). *Environmental Chemistry*
416 *Letters* 8, 39-44.
417

418 Harrison, R.M., Smith, D.J.T., Luhana, L. 1996. Source apportionment of atmospheric polycyclic
419 aromatic hydrocarbons collected from an urban location in Birmingham, UK. *Environmental*
420 *Science & Technology* 30, 825-832.
421

422 Hassan, S.K., Khoder, M.I., 2012. Gas-particle concentration, distribution, and health risk
423 assessment of polycyclic aromatic hydrocarbons at a traffic area of Giza, Egypt. *Environmental*
424 *Monitoring & Assessment* 184, 3593-3612.
425

426 IARC, 2010. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Volume
427 92, Some Non-Hetrocyclic Polycyclic Aromatic Hydrocarbons and Some Related Exposures, World
428 Health Organization International Agency for Research on Cancer, Lyon, France.
429

430 Jang, E., Alam, M.S., Harrison, R.M., 2013. Source apportionment of polycyclic aromatic
431 hydrocarbons in urban air using Positive Matrix Factorization and spatial distribution analysis.
432 *Atmospheric Environment* 79, 271-285.

433 Keyte, I.J., Harrison, R.M., Lammel, G., 2013. Chemical reactivity and long-range transport
434 potential of polycyclic aromatic hydrocarbons - A review. *Chemical Society Reviews* 42, 9333-
435 9391.
436

437 Kim, K., Jahan, S.A., Kabir, E., Brown, R.J.C., 2013. A review of airborne polycyclic aromatic
438 hydrocarbons (PAHs) and their human health effects. *Environment International* 60, 71-80.
439

440 Mari, M., Harrison, R.M., Schuhmacher, M., Domingo, J.L., Pongpiachan, S., 2010. Inferences
441 over the sources and processes affecting polycyclic aromatic hydrocarbons in the atmosphere
442 derived from measured data. *Science of the Total Environment* 408, 2387-2393.
443

444 Mastral, A.M., Callen, M.S., 2000. A review on polycyclic aromatic hydrocarbon (PAH) emissions
445 from energy generation. *Environmental Science & Technology* 34, 3051-3057.
446

447 Pies C., Joffmann, B., Petrowsky, J., Yang, Y., Ternes, T.A., Hofmann, T., 2008. Characterization
448 and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils.
449 *Chemosphere* 72, 1594-1601.

- Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmospheric Environment* 42, 2895-2921.
- Sun, F., Lifflejohn, D. and Gibson, M.D., 1998. Ultrasonication extraction and solid phase extraction clean-up for determination of US EPA 16 priority pollutant polycyclic aromatic hydrocarbons in soils by reversed-phase liquid chromatography with ultraviolet absorption detection. *Analytica Chimica Acta* 364, 1-11.
- Tobiszewski, M., Namiesnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. *Environmental Pollution* 162, 110-119.
- Trasande, L., Urbina, E.M., Khoder, M., Alghamdi, M., Shabaj, I., Alam, M.S., Harrison, R.M., Sham, M., 2015. Polycyclic aromatic hydrocarbons, brachial artery distensibility and blood pressure among children residing near an oil refinery. *Environmental Research* 136, 133-140.
- Wang, F., Lin, T., Feng, J., Fu, H., Guo, Z., 2015. Source apportionment of polycyclic aromatic hydrocarbons in PM_{2.5} using positive matrix factorization modeling in Shanghai, China. *Environmental Science Processes Impacts* 17, 197-205
- WHO, 2000. Air Quality Guidelines for Europe, Second Edition, World Health Organisation, Regional Office for Europe, Copenhagen, Denmark.
- WHO, 2010. WHO Guidelines for Indoor Air Quality: Selected Pollutants, World Health Organization, Regional Office for Europe, Copenhagen, Denmark.
- Xie, M., Barsanti, K.C., Hannigan, M.P., Dutton, S.J., Vedal, S. 2013. Positive matrix factorization of PM_{2.5} – eliminating the effects of gas/particle partitioning of semivolatile organic compounds. *Atmospheric Chemistry & Physics* 13, 7381-7393.
- Yamasaki, H., Kuwata, K., Miyamoto, H., 1982. Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. *Environmental Science & Technology* 16, 189-194.
- Yunker M.B., Macdonald, R.W., Vingarzan, R., Michell, H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry* 33, 489-515.
- Zhao, B., Zhang, S., Zhou, Y., He, D., Li, Y., Ren, M., Xu, Z., Fang, J., 2105. Characterization and quantification of PAH atmospheric pollution from a large petrochemical complex in Guangzhou: GC-MS/MS analysis. *Microchemistry Journal* 119, 140-144.

490 **TABLE LEGENDS**

491
492 **Table 1:** Total concentrations of PAH congeners at all sites (ng m^{-3})

493
494 **Table 2:** (a) Coefficients of Divergence (COD) values for total PAH for sites A, B and C1
495 (first campaign); (b) COD values for total PAH for sites D, E and C2 (second
496 campaign).

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498
499 **FIGURE LEGENDS**

500
501 **Figure 1:** Locations of sampling sites and the city of Jeddah. The sites are: A-refinery; B-ring
502 road; C-Abhur; D-Rabegh and E-Rayes.

503
504 **Figure 2:** Average congener profile of PAH from both sampling campaigns at the five sites,
505 including both campaign data for Site C.

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507 **Figure 3:** Air mass back trajectories to the the three sites for 17 September 2013 ending at 950
508 mb showing the air mass running parallel to the Red Sea coast.

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511 only air samples when the air mass travelled from north-west to south-east parallel to
512 the Red Sea coast.

513

Table 1: Total concentrations of PAH congeners at all sites (ng m⁻³).

Congener	Site A		Site B		Site C1		Site C2		Site D		Site E	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Fluorene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.47	0.20-1.54	0.90	0.45-1.92	1.13	0.36-6.98
Phenanthrene	21.15	11.63-41.55	16.83	5.75-29.67	8.65	2.71-21.91	6.03	2.57-12.09	7.97	4.51-14.41	9.58	3.24-29.92
Anthracene	1.43	0.40-4.14	1.63	0.57-3.13	0.71	0.17-1.65	0.31	0.14-0.79	0.46	0.20-1.30	0.82	0.19-7.53
Fluoranthene	3.47	1.01-7.77	2.69	1.22-4.79	1.11	0.40-2.42	0.94	0.50-1.67	1.23	0.69-2.53	1.18	0.40-5.86
Pyrene	6.23	1.43-15.30	4.15	1.85-8.06	0.82	0.32-1.44	0.89	0.43-1.50	1.45	0.79-2.51	1.11	0.27-7.08
Retene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.56	0.05-1.14	0.47	0.16-1.09	0.52	0.21-1.75
Benzo(a)anthracene	0.23	0.07-0.79	0.24	0.08-0.33	0.06	0.02-0.23	0.26	0.05-0.59	0.37	0.04-1.00	0.37	0.02-1.48
Chrysene	0.65	0.20-2.27	0.61	0.26-1.03	0.17	0.06-0.60	0.26	0.07-0.47	0.28	0.02-0.61	0.39	0.06-1.91
Benzo(b)fluoranthene	0.57	0.17-1.11	0.47	0.22-0.81	0.12	0.03-0.42	0.12	0.01-0.25	0.16	0.05-0.25	0.23	0.04-1.53
Benzo(k)fluoranthene	0.60	0.19-1.24	0.42	0.23-0.71	0.11	0.03-0.37	0.12	0.02-0.23	0.15	0.02-0.25	0.24	0.04-2.08
Benzo(e)pyrene	0.60	0.17-1.30	0.50	0.24-0.82	0.13	0.04-0.42	0.10	0.01-0.27	0.11	0.02-0.29	0.19	0.03-1.68
Benzo(a)pyrene	0.39	0.09-1.01	0.30	0.12-0.56	0.09	0.02-0.30	0.07	0.00-0.16	0.09	0.01-0.14	0.16	0.01-1.53
Indeno(1,2,3-cd)pyrene	0.63	0.22-1.21	0.47	0.26-0.75	0.11	0.02-0.38	0.09	0.01-0.17	0.09	0.02-0.29	0.18	0.03-1.89
Dibenz(a,h)anthracene	0.15	0.04-0.27	0.09	0.04-0.14	0.02	0.01-0.07	0.03	0.00-0.08	0.04	0.01-0.12	0.08	0.01-0.67
Benzo(ghi)perylene	1.27	0.46-2.38	1.03	0.51-1.61	0.17	0.03-0.64	0.11	0.02-0.32	0.18	0.04-0.69	0.24	0.04-2.32
Coronene	0.79	0.29-1.59	0.61	0.32-0.88	0.09	0.01-0.36	0.09	0.03-0.21	0.16	0.04-0.45	0.20	0.06-1.54

Note : Sites A, B and C1 refer to the first campaign (Alghamdi et al. 2015a). Sites C2 (Abhur), D (Raybegh) and E (Rayes) refer to the second campaign.

: n.d. = not determined

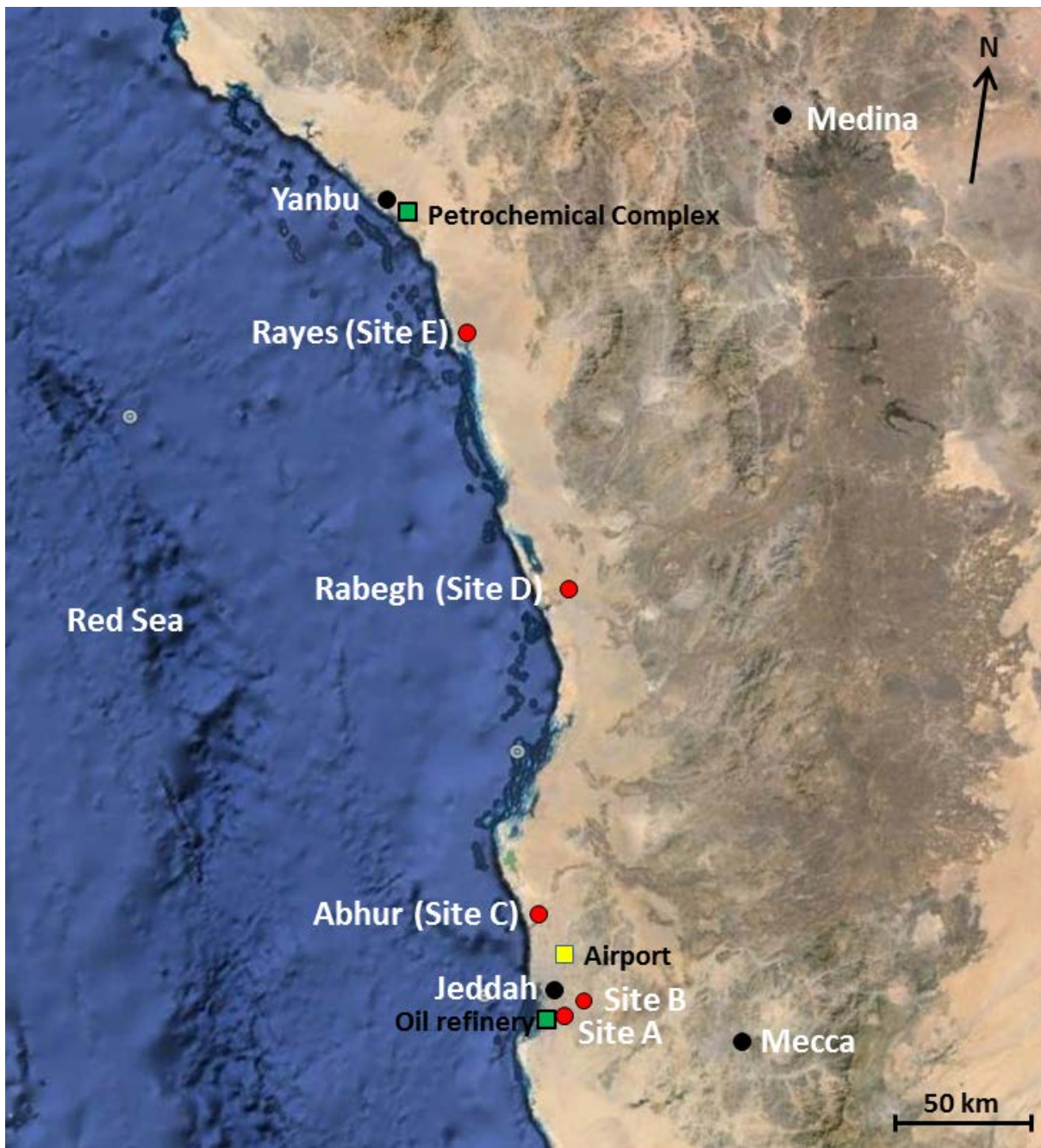
Table 2: (a) Coefficients of Divergence (COD) values for total PAH congeners for sites A, B and C1 (first campaign); (b) COD values for total PAH for sites C2, D and E (second campaign).

(a)

Species	COD _{A&B}	COD _{A&C1}	COD _{B&C1}
Phenanthrene	0.250	0.459	0.433
Anthracene	0.313	0.464	0.518
Fluoranthene	0.374	0.543	0.493
Pyrene	0.406	0.728	0.676
Benzo(a)anthracene	0.399	0.611	0.691
Chrysene	0.348	0.607	0.654
Benzo(b)fluoranthene	0.227	0.685	0.674
Benzo(k)fluoranthene	0.272	0.724	0.677
Benzo(e)pyrene	0.269	0.671	0.680
Benzo(a)pyrene	0.296	0.675	0.677
Indeno(1,2,3-cd)pyrene	0.237	0.749	0.723
Dibenz(a,h)anthracene	0.356	0.769	0.677
Benzo(ghi)perylene	0.227	0.806	0.793
Coronene	0.238	0.828	0.810

(b)

Species	COD _{C2&D}	COD _{C2&E}	COD _{D&E}
Fluorene	0.430	0.398	0.314
Phenanthrene	0.250	0.474	0.253
Anthracene	0.261	0.413	0.316
Fluoranthene	0.188	0.456	0.361
Pyrene	0.291	0.480	0.447
Benzo(a)anthracene	0.414	0.471	0.342
Chrysene	0.485	0.558	0.453
Retene	0.292	0.402	0.331
Benzo(b)fluoranthene	0.155	0.305	0.374
Benzo(k)fluoranthene	0.196	0.388	0.387
Benzo(e)pyrene	0.287	0.465	0.370
Benzo(a)pyrene	0.320	0.472	0.332
Indeno(1,2,3-cd)pyrene	0.273	0.468	0.385
Dibenz(a,h)anthracene	0.364	0.564	0.408
Benzo(ghi)perylene	0.376	0.482	0.353
Coronene	0.363	0.462	0.333



1
2 **Figure 1:** Locations of sampling sites and the city of Jeddah. The sites are: A-refinery; B-ring
3 road; C-Abhur; D-Rabegh and E-Rayes.
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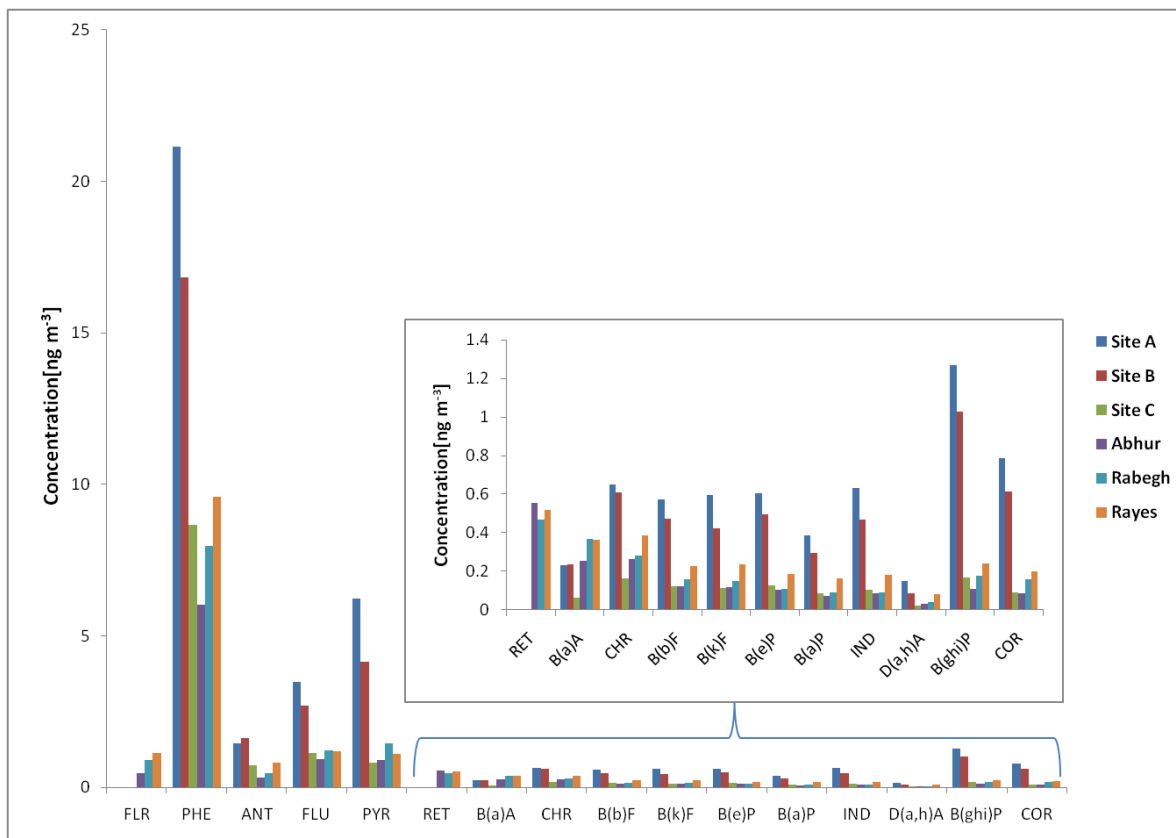
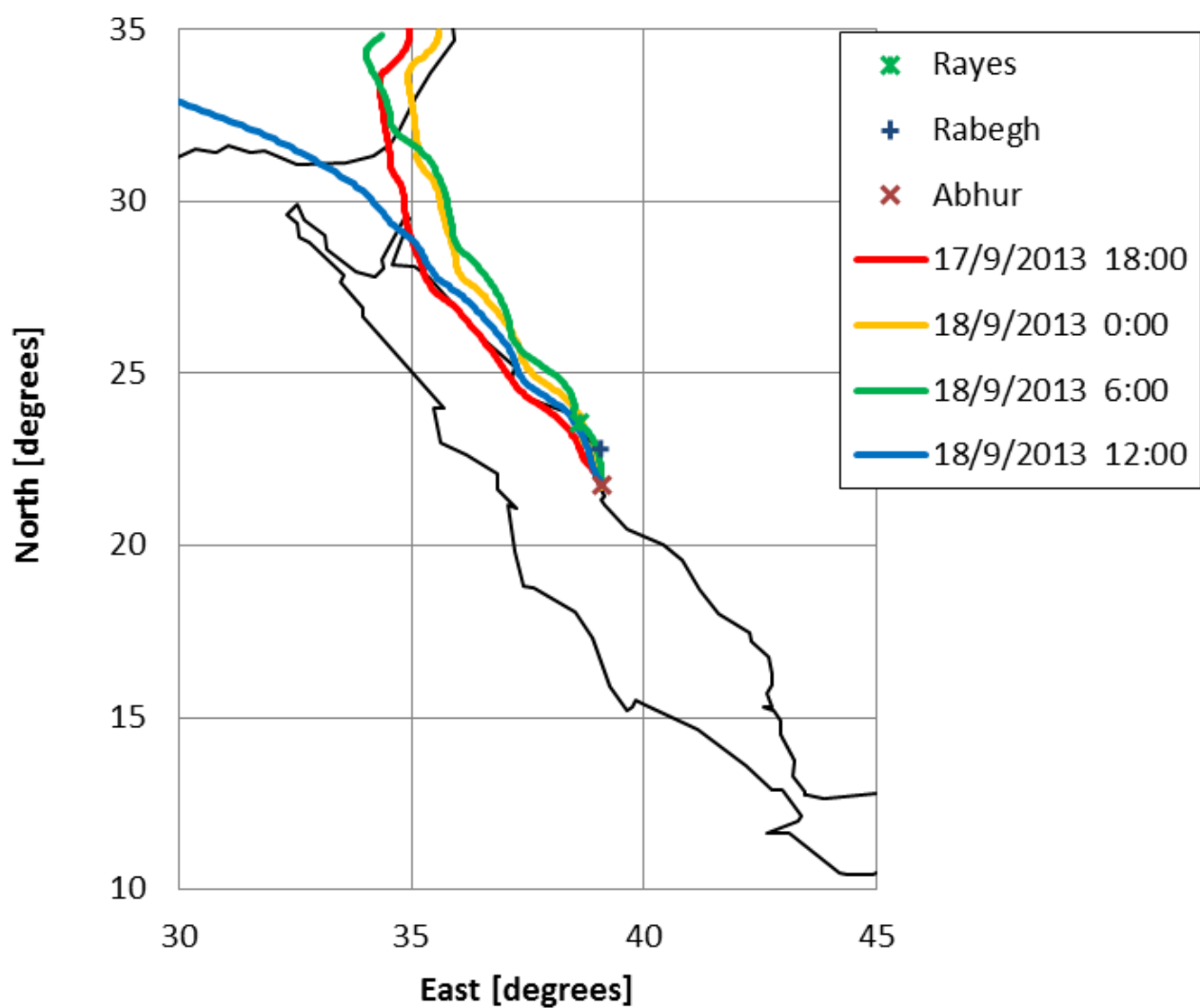


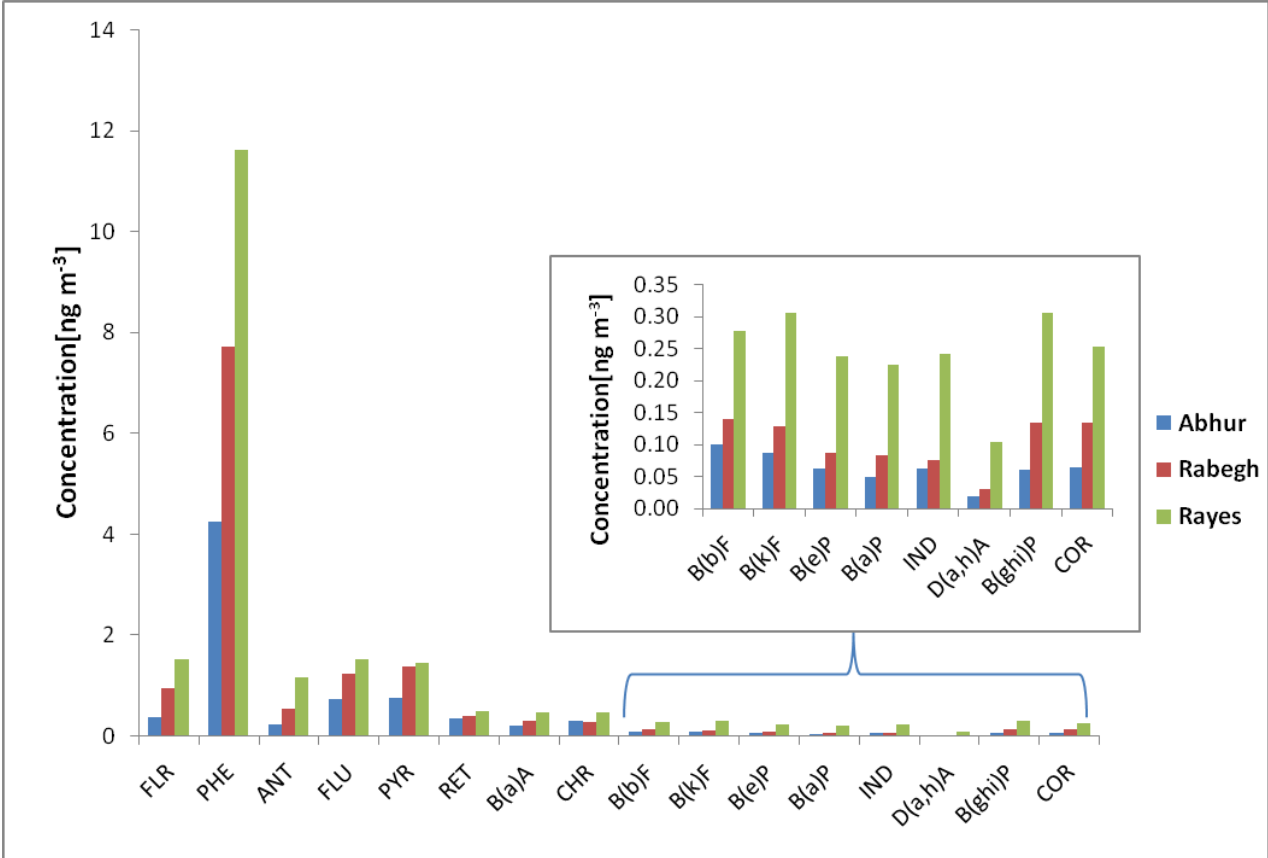
Figure 2: Average congener profile of PAH from both sampling campaigns at the five sites, including both campaign data for Site C. The site C data refer to the first campaign (1) and the Abhur data refer to the second campaign (2).



12

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17

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19 samples when the air mass travelled from north-west to south-east parallel to the Red Sea coast.
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